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Formation of acidic Brönsted $(MoO_x)^-(H_y)^+$ evidenced by XRD and 2,6-lutidine FTIR spectroscopy for cumene cracking



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ABSTRACT

2,6-Lutidine adsorbed IR spectroscopy has been employed to study the property of acidic sites on MoO₃ and Pt/MoO₃. The results showed that both catalysts possess doublet adsorption bands at 1605+1585 cm⁻¹, ascribed to Lewis acid sites, and duo-doublet bands at 1660+1650 and 1640+1630 cm⁻¹, ascribed to hydroxyl groups; these indicate an —OH defect structure of MoO₃ and Mo–OH Brönsted acidic sites. All Brönsted acid sites were strong enough to retain outgassing at 473 K, while a considerable number of relatively weak and medium acid sites as well as strong Lewis acid sites existed. The addition of Pt slightly altered the ratio of Lewis/Brönsted acid sites and distribution of Lewis acid sites. The XRD result confirmed the formation of molybdenum oxyhydride $(MOO_x)^-(H_y)^+$ on the hydrogen treated Pt/MoO₃, whereas the hydrogen adsorption on 2,6-lutidine pre-adsorbed catalysts showed the formation of protonic acid sites over Pt/MoO₃. These results strongly suggested that the interaction of molecular hydrogen with Pt/MOO₃ formed acidic Brönsted $(MOO_x)^-(H_y)^+$ via a hydrogen spillover mechanism. In fact, no $(MOO_x)^-(H_y)^+$ and protonic acid sites were observed on Pt-free MoO₃. The presence of $(MOO_x)^-(H_y)^+$ enhanced the activity of Pt/MoO₃ in the cumene hydrocracking in which the rate conversion of cumene increased by about 30%, while the apparent activation energy decreased by approximately 28 kJ/mol.

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1. Introduction

Recently, solid acid catalysts based on Al_2O_3 , zeolite, ZrO_2 , and MoO_3 have been explored widely due to stability and regenerative properties and the fact that they are highly active at a wide range of reaction temperatures [1–3]. Bifunctional catalysts consisting of acidic oxides and noble metals showed high efficiency in the acid catalytic reaction, such as alkylation, isomerization and cracking. An acid catalytic reaction is normally carried out in the presence of hydrogen due to the role of hydrogen in the formation of protonic acid sites and the removal of coke deposits from the surface catalysts [4–6]. For certain classes of catalyst, the presence of a noble metal is indispensable in the interaction with molecular hydrogen, which leads to the formation of protonic acid sites [7,8].

Recently, several research groups have extensively focused on the study of MoO_3 type catalysts for acid catalytic reactions. Blekkam et al. reported that the treatment of MoO_3 with H_2 /alkane

mixture yielded an active and selective catalyst for hexane isomerization [9,10]. They concluded, based on the XRD, XPS and HRTEM results, that a molybdenum compound containing carbon as an oxycarbide (MoO_xC_y) acts as an active phase for alkane isomerization. In addition, Ledoux and co-workers showed that oxygen-modified Mo₂C and carbon-modified MoO₃ were active and selective for heptane isomerization [10,11]. Molybdenum oxycarbide, which is formed by incorporating carbon atoms in the molybdenum oxide lattice, has been considered to be the active phase for heptane isomerization. Katrib et al. suggested that the MoO₂ phase was responsible for hexane isomerization in which the isomerization of MoO₂ proceeds via a bifunctional mechanism [12]. In contrast, Wehrer et al. pointed out that MoO has been proposed to act as the active phase for alkane isomerization after incomplete reduction with pure H₂ [13–15], and the catalytic activity of partially-reduced MoO₃ was strongly dependent on the reduction temperature [16]. In addition to the molybdenum oxide species, Matsuda et al. reported that H₂-reduced MoO₃ was accompanied by an increase in the surface area and became an active and selective catalyst for heptane isomerization [3]. The surface area can be markedly enlarged when MoO₃ is reduced through the formation of a hydrogen molybdenum bronze H_xMoO_3 phase. Recently, they also studied the effects of H₂ reduction on MoO₃, Pt/MoO₃

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and H_xMoO_3 , in which the samples were prepared by a mixture of MoO₃, Zn and HCl solution [17]. Based on the XRD results, the effects of H_2 reduction on H_xMoO_3 were similar to those on Pt/MoO₃, but different from those on MoO₃; H₂ reduced H_xMoO₃ and Pt/MoO₃ consisted of MoO_xH_y and Mo metal in which both reduced H_xMoO_3 and Pt/MoO₃ were active in the alkane isomerization. In addition, MoO₃ was converted to a mixture of MoO₂ and Mo metal. Although the type of acidic sites was not distinguished clearly, NH₃-TPD results showed that the reduction of H_xMoO_3 formed acidic MoO_xH_y , which was active in the isomerization [18]. Matsuda et al. suggested that the generation of isomerization activity could be related to reduction of H_xMoO_3 to MoO_xH_y , and showed that more acidic MoO_xH_y can be formed from H_xMoO_3 with a larger hydrogen content [18]. The formation of active MoO_xH_y for isomerization was also reported over SiO₂ [19] and TiO₂ [12] supports. Al-Kandari and co-workers explored bifunctional (metal-acid) catalysts based on titanium oxides for alkane isomerization [20]. They reported that the H₂-reduction of MoO₃/TiO₂ at 673 K for 12 h led to the formation of bifunctional (metal-acid) MoO_{2-x} (OH)_v phase structure on the surface of TiO₂. They performed the characterization of reduced $\rm MoO_3/TiO_2$ by XPS-UPS, ISS, FTIR and XRD techniques and showed that the metallic-acidic property of the MoO_{2-x} (OH)_y phase promoted high catalytic activity toward the isomerization of *n*-hexane, *n*-heptane and *n*-octane [20–23].

Although several reports have been published on MoO₃-type catalysts, there is a lack of reports regarding the study of acidic properties, the effect of hydrogen in the acidity and the activity of MoO₃ type catalysts. In the present report, we demonstrate the results of XRD, ESR, IR and acid-catalytic cumene hydrocracking on MoO₃ and Pt/MoO₃ catalysts. The adsorption of 2,6-lutidine probe molecules was monitored by IR spectroscopy in order to study the acidic nature and acid strength distribution of the catalysts. In contrast, the interaction of hydrogen with catalyst was assessed based on the XRD, ESR and 2,6-lutidine pre-adsorbed IR spectroscopy in order to confirm the formation and role of the acidic Brönsted (MoO_x)⁻(H_y)⁺ phase on the surface of MoO₃-type catalysts.

2. Experimental

The MoO₃ sample was prepared by calcination of H_2MoO_4 (Merck) at 673 K for 3 h. The Pt/MoO₃ was prepared by impregnation of MoO₃ with an aqueous solution of H_2PtCl_6 (Merck) followed by calcinations at 673 K in air. The surface areas of MoO₃ and Pt/MoO₃ were 58 and 65 m²/g, respectively. The content of Pt was 0.5 wt%.

Crystalline phases of H₂-reduced samples were determined by X-ray diffraction (XRD) recorded on a Bruker AXS D8 Automatic Powder Diffractometer using Cu K α radiation source with $\lambda = 1.5418$ Å at 40 kV and 40 mA over a range of $2\theta = 20^{\circ}-60^{\circ}$ with a step size = 0.1. Samples for XRD measurements were prepared as follows: a sample was subjected to H₂ reduction at 673 K for 1, 3 and 6 h. After cooling to room temperature under H₂ flow, the reduced sample was dispersed in *n*-heptane solution to avoid any bulk oxidation. The BET surface area and total pore volume of the samples were determined by N₂ adsorption–desorption isotherm using a Quantachrome Autosorb-1 at 77 K. Prior to the measurement, the sample was outgassed at 573 K for 3 h.

Fourier Transform Infra-Red (FTIR) measurements were carried out with Agilent Carry 640 FTIR spectrometer. Before the analysis, catalysts were activated according to the method described in the literature [24]. In brief, a self-supported wafer placed in an *in situ* stainless steel IR cell with CaF_2 windows was activated with a hydrogen flow at 673 K for 3 h, followed by outgassing at 673 h for 3 h. For 2,6-lutidine adsorption, the activated catalyst was exposed to 0.53 kPa of 2,6-lutidine at room temperature for 15 min followed by outgassing at room temperature, 373 and 473 K for 15 min, respectively.

For the observation of the generation of protonic acid sites from molecular hydrogen on the catalysts, the 2,6-lutidine preadsorbed catalyst was exposed to 13.33 kPa of hydrogen at room temperature. Then, the catalyst was heated up stepwise from room temperature to 373 K. The spectra were recorded at room temperature.

A JEOL JES-FA100 ESR spectrometer was used to observe the formation of electron holes or unpaired electrons in vacuo heating, and to observe the interaction of the electron holes or unpaired electrons with electrons formed from molecular hydrogen through a hydrogen-spillover mechanism from room temperature to 473 K. Prior to the measurement, the catalyst was activated in the presence of hydrogen at 673 K for 3 h, followed by outgassing at 673 K for 3 h. Then the activated catalyst was exposed to 13.33 kPa gaseous hydrogen at room temperature. The catalyst then was heated to 323, 373, 423 and 473 K in the presence of hydrogen. All spectra were recorded at room temperature.

The cumene cracking reaction was carried out at 573 K in a microcatalytic pulse reactor equipped with an online sampling valve for gas chromatography analysis. Prior to the reaction, the catalyst was activated in an oxygen stream at 673 K for 1 h. The catalyst was subsequently heated in a hydrogen stream at 673 K for 6 h and then cooled to a reaction temperature in a hydrogen stream. A dose of cumene (43 μ mol) was passed over the 0.4 g of activated catalyst, and the products were trapped at 77 K before being flash-evaporated into an online 6090N Agilent gas chromatograph equipped with a VZ-7 packed column, FID and TCD detectors. The intervals between doses were kept constant at 30 min.

The selectivity to particular product (S_i) and conversion of reactant (X_{reactant}) were calculated according to Eqs. (1) and (2), respectively.

$$S_{i}(\%) = \frac{C_{i}}{\sum C_{i} - C_{\text{reactant}}} \times 100$$
(1)

$$X_{\text{reactant}} = \frac{\sum C_{\text{i}} - C_{\text{reactant}}}{\sum C_{\text{i}}}$$
(2)

where C_i and $C_{reactant}$ are mole numbers of a particular compound and for residual reactant, respectively, which were calculated based on the Scott hydrocarbon calibration standard gas (Air Liquide America Specialty Gases LLC). The specific rate conversion data was obtained by multiplication of the differential conversion data and rate constant (k). The rate constant was determined by the molar concentration of the reactant divided by mass of the catalyst per unit time with the assumption that the retention time for reactant in the catalyst bed was negligibly small.

3. Results and discussion

Fig. 1A and B illustrates the change in the XRD patterns of MoO₃ and Pt/MoO₃ after heating in hydrogen flow at 673 K for 1, 3 and 6 h, respectively. The diffraction lines corresponding to MoO₃ (JCPDS data file 05-0508) were observed for both untreated MoO₃ and Pt/MoO₃ (data not shown). The hydrogen treatment of MoO₃ evolved the phase of Mo sites, in which MoO₂ phase was observed after 1 h. New diffraction lines appeared at $2\theta = 25.8^{\circ}$, 36.7° and 53.3° after 3 h and the line still remained even after 6 h, Fig. 1A. For Pt/MoO₃, the diffraction lines due to MoO₃ phase disappeared completely and the lines at $2\theta = 25.8^{\circ}$, 36.7° and 53.3° corresponding to MoO₂ phase were observed after hydrogen treatment for 1 h. The intensity of MoO₂ decreased continuously with the treatment time and small diffraction lines still remained after 6 h. After 6 h, new diffraction lines at $2\theta = 38.1^{\circ}$ and 44.3° corresponding

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8-16



Fig. 1. XRD pattern of (A) MoO₃ and (B) Pt/MoO₃ reduced by H₂ at 673 K for (a) 1 h (b) 3 h and (c) 6 h. (*) MoO₃, (\bullet) MoO₂, and (\blacktriangle) (MoO₃)⁻(H_y)⁺ phase.

to the molybdenum oxyhydride phase (MoO_xH_y) were observed [16,18]. In recent years, several research groups have studied the diffraction pattern of MoO_xH_y . Ledoux et al. [25] and Delporte et al. [26] suggested that the diffraction lines of MoO_3 at $2\theta = 38.1^\circ$ and 44.3° correspond to the presence of MoO_xH_y , which is analogous to molybdenum oxycarbide, MoO_xC_y . In addition, Matsuda et al. reported that the diffraction lines at $2\theta = 38.1^\circ$ and 44.3° correspond to the MoO_xH_y phase [18]. In contrast, Wehrer et al. [13–15] pointed out that the presence of hydrogen in this compound was hard to accept because thermal treatment did not change the XRD pattern, and they proposed the existence of reduced molybdenum oxide with the composition close to MoO. Moreover, Hawkins and Worrel assigned the diffraction lines at $2\theta = 38.1^\circ$ and 44.3° to a Mo_2O species [27].

Fig. 2 shows the adsorption–desorption isotherms of MoO_3 and Pt/MoO_3 samples. No appreciable difference appeared in the pore size distribution between MoO_3 and Pt/MoO_3 catalysts.

The adsorption–desorption isotherms of MoO₃ were identical to Pt/MoO₃, with both samples displaying the type IV isotherms with a type H4 hysteresis loop in accordance with IUPAC adsorption isotherm recommendations, indicating a complex mesoporous structure. Fig. 2A shows that, at higher relative pressure (P/P_0 between 0.5 and 0.8), a notable increase of adsorbed nitrogen was observed, suggesting an important external surface area contribution. The presence of Pt did not change the distribution of the mesopores, with both catalysts giving similar pore volume due to small addition of Pt metal (as shown in Fig. 2B).

The nature of the acid sites in the MoO₃ and Pt/MoO₃ was qualitatively probed by 2,6-lutidine adsorption monitored by IR spectroscopy. 2,6-Lutidine (pK_b = 7.4), which demonstrated a more basic character than the pyridine (pK_b = 8.8), is used to study the acidic nature of catalysts and their changes induced by the presence of molecular hydrogen. The easiness of 2,6-lutidine to produce protonated species and weaker affinity for Lewis acid sites (due to the



Fig. 2. (A) Nitrogen adsorption isotherm for MoO₃ and Pt/MoO₃ with black symbol (adsorption) and white adsorption (desorption) and (B) adsorption pore volume for MoO₃ and Pt/MoO₃.

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8-16



Fig. 3. IR spectra of 2,6-lutidine adsorbed on MoO₃ and Pt/MoO₃. Brönsted acid site region at 1675–1615 cm⁻¹, and Lewis acid site region at 1630–1555 cm⁻¹ when 2,6-lutidine is adsorbed at room temperature. Solid line: experimental spectra; dotted line: reconstituted spectra.

steric hindrance induced by the methyl group) give better interaction toward relatively weak Brönsted and strong Lewis acid sites [28]. Fig. 3 shows IR spectra of 2,6-lutidine adsorbed on MoO₃ and Pt/MoO₃ at room temperature in the region of 1550–1700 cm⁻¹ and their Gaussian curve-fitting. For both catalysts, 2,6-lutidine probe molecule was able to interact strongly with Brönsted and Lewis acidic sites at room temperature. Two characteristic absorbance bands arose below and above 1620 cm⁻¹, which are ascribed to the 2,6-lutidine species adsorbed on Lewis and Brönsted acid sites, respectively. These bands are more clearly seen by

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8-16

A B 1605 cm⁻¹ 1605 cm⁻¹ 1650 cm⁻¹ 1650 cm⁻¹ 1585 cm⁻¹ 1585 cm 1630 cm 1630 cm (e) (e) Adsorbance Absorbance (d) (d) (c (c)(b) (\overline{b}) (a) (a) 0.2 0.2 1600 1700 1650 1600 1550 1700 1650 1550 Wavenumber [cm⁻¹] Wavenumber [cm⁻¹]

Fig. 4. IR spectra of 2,6-lutidine adsorbed on (A) MoO₃ and (B) Pt/MoO₃ at (b) room temperature, followed by heating in a vacuum at (c) room temperature, (d) 373 K, (e) 473 K. (a) Before exposure to 2,6-lutidine.

Gaussian curve-fitting. Both catalysts showed dual doublet adsorption bands at 1660 + 1640 and 1650 + 1630 cm⁻¹, which are associated with the 8a and 8b mode of lutidinium cations on the hydroxyl group (-OH) defect structure of MoO₃ and protonated 2,6-lutidine adsorbed on Brönsted acid sites, which formed as Brönsted (Mo–OH) acidic function [23]. Also, Lewis acid sites are more abundant on both catalysts than that of Brönsted acid sites. The ratio of Lewis to Brönsted acid sites of Pt/MoO₃ was slightly higher than that of Pt-free MoO₃. The intensification of Lewis acid sites in the presence of Pt may be caused by the enhancement in the dehydroxylation or dehydration process leaving Lewis acid sites. A similar phenomenon was also observed on our previous assignment on Pt/WO₃–ZrO₂ in which the introduction of Pt resulted in an increase in the ratio of Lewis acid sites to Brönsted acid sites due to enhancement in the removal of OH groups [8]. We also reported the alteration in the acidic sites on ZrO_2 due to the introduction of a small amount of MoO_3 [29]. The IR spectra of adsorbed 2,6-lutidine showed that the introduction of 5 wt% MoO_3 to ZrO_2 partially eliminated the absorbance band at 1605 cm⁻¹ and developed new absorbance bands at 1595 and 1590 cm⁻¹. The elimination of the absorbance band at 1605 cm⁻¹ might be related to the interaction of MoO_3 with Lewis acid sites corresponding to the monoclinic phases of ZrO_2 , resulting in the development of new Lewis acidic center with different strengths. However, in the case of MoO_3/Al_2O_3 , a low concentration of MoO_3 (approximately 1.25 atoms/nm²) did not significantly affect the number of acid sites of Al_2O_3 . At high loadings of MoO_3 (approximately 3.5 atoms/nm²), the number of surface Lewis sites appreciably decreased and surface Brönsted acid sites were formed [30].



Fig. 5. IR spectra of 2,6-lutidine on MoO₃ (A) and Pt/MoO₃ (B) when 2,6-lutidine pre-adsorbed catalysts were heated in hydrogen at (b) room temperature, (c) 323 K, (d) 338 K, (e) 348 K, and (f) 373 K. (a) Before exposure to hydrogen.

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8–16



Fig. 6. (A) and (C) Absorbance of IR bands at Lewis acid sites on MoO₃ and Pt/MoO₃. (B) and (D) Absorbance of IR bands at Brönsted acid sites on MoO₃ and Pt/MoO₃. Brönsted acid sites at (\triangle) 1660 cm⁻¹; (\triangle) 1640 cm⁻¹ and (\blacksquare) 1650 cm⁻¹; (\square) 1630 cm⁻¹. Lewis acid sites at (\bigcirc) 1605 cm⁻¹ and (\bigcirc) 1585 cm⁻¹. (\Diamond) Before exposure to hydrogen.

Fig. 4 shows the IR spectra of 2,6-lutidine adsorbed on MoO₃ (A) and Pt/MoO₃ (B) in the function of 2,6-lutidine outgassing temperature. Upon raising the outgassing temperature, 2,6-lutidine molecules adsorbed on weak acid sites should be desorbed at lower temperature, and those adsorbed on strong acid sites should be desorbed at higher temperature. For both catalysts, the absorbance bands associated with Brönsted acid sites did not change much with the outgassing temperature up to 473 K, while the absorbance bands ascribed to Lewis acid sites decreased considerably with increasing temperature. These results indicated that most of the Brönsted acid sites were strong enough to retain 2,6-lutidine against outgassing at 473 K, while a considerable number of relatively weak and medium acid sites as well as strong Lewis acid sites existed. It should be noted that the decrease in the Lewis acid sites at higher outgassing temperature was extensively observed on Pt/MoO₃ than that of MoO₃. This may be due to the desorption of adsorbed 2,6-lutidine was accelerated by the presence of Pt.

Fig. 5 shows the changes of IR spectra in the range of $1700-1550 \,\mathrm{cm}^{-1}$ when the 2,6-lutidine pre-adsorbed MoO₃ was heated in the presence of hydrogen from room temperature up to 373 K. Since the 2,6-lutidine pre-adsorbed sample was outgassed at 473 K, the acid sites under consideration are only strong acid sites that 2,6-lutidine can retain at outgassing temperature of 473 K

and below. For MoO₃ (Fig. 5A), increasing the temperature did not significantly change the intensity of both acid sites. However, heating of 2,6-lutidine pre-adsorbed Pt/MoO₃ in the presence of hydrogen gradually changed the absorbance bands corresponding to both Lewis and Brönsted acid sites (Fig. 5B). The intensity of Lewis acid sites decreased and the intensity of Brönsted acid sites increased with heating temperature. The changes of the absorbance bands for both Lewis and Brönsted acid sites caused by interaction with hydrogen gas for both catalysts are plotted against the heating temperature in Fig. 6. As the heating temperature of MoO₃ was raised, a small increase was observed at the doublet band 1605+1585 cm⁻¹ corresponding to the Lewis acidic centers and there was almost no change in the absorbance bands at 1660 + 1640 and 1650 + 1630 cm⁻¹ attributed to the Brönsted acid sites (Fig. 6A and B). The increase in the intensity of Lewis acid sites may be related to the formation of the MoO₂ phase during hydrogen treatment. In contrast, Fig. 6C and D show the different hydrogen $treatment\,effect\,on\,Pt/MoO_3\,catalysts.\,Doublet\,absorbance\,bands\,at$ $1605 + 1585 \text{ cm}^{-1}$ corresponding to the Lewis acidic center began to decrease at 323 K, while dual doublet bands corresponding to Brönsted acid sites at 1660 + 1640 and 1650 + 1630 cm⁻¹ began to increase at 323 K and the changes occurred extensively with the increasing temperature. The doublet bands at 1660+1640 cm⁻¹

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8-16



Fig. 7. ESR spectra of (A) MoO₃ and (B) Pt/MoO₃ sample in hydrogen atmosphere. The sample was heated in hydrogen at (c) room temperature, (d) 323 K, (e) 373 K, (f) 423 K, and (g) 473 K. (a) ESR spectrum before outgassed and (b) after activated at 673 K.

did not increase much above 323 K, while the doublet bands at 1650 + 1630 cm⁻¹ increased continuously with temperature showing dependency relations of the formation of protonic acid sites (Mo-OH) from molecular hydrogen and heating temperature. These results also revealed the indispensability of Pt metal on MoO₃ to facilitate the formation of acidic Brönsted Mo-OH, thereby producing of acidic Brönsted $(MoO_x)^-(H_y)^+$. In fact, no formation of acidic Brönsted $(MoO_x)^-(H_y)^+$ was observed on Pt-free MoO₃. The necessity of the metals like Pt or Pd on solid acid catalyst has also been reported on SO42--ZrO2 [31] and HZSM-5 [32] catalysts. Contrarily, the presence of Pt or Pd metal is dispensable on WO₃-ZrO₂ [33] and MoO₃-ZrO₂ [29] catalysts due to the ability of W or Mo or acidic sites to adsorb and to dissociate molecular hydrogen to form atomic hydrogen. In addition, we have studied the interaction of molecular hydrogen with MoO₃ and Pt/MoO₃ quantitatively with almost no interaction between hydrogen and MoO₃ without Pt metal [34]. The results are essentially the same with SO_4^{2-} -ZrO₂ catalysts in which the presence of Pt largely enhanced the hydrogen uptake capacity of supports. These results of hydrogen uptake on MoO₃ types are in good agreement with our IR results where H₂-reduced MoO₃ formed MoO₂; in tandem, H₂reduced Pt/MoO₃ formed acidic Brönsted $(MoO_x)^-(H_y)^+$. Several research groups have studied the formation of molybdenum oxyhydride induced by hydrogen treatment. Based on the XRD data, Matsuda and co-workers reported the formation of MoO_xH_y phase on the H₂ reduced H_xMoO₃ and Pt loaded on MoO₃ [17], while Al-Kandari et al. studied the acid function Brönsted Mo-OH group on MoO₃/TiO₂ catalyst by pyridine adsorbed IR. There are two bands adsorption at 1636 and 1536 cm⁻¹ distinguished for the presence of pyridinium ions (pyH⁺) on Brönsted acid sites. They stated the metallic function to be the initial state for the dissociation of hydrogen molecules into active hydrogen atoms, which are then bonded to surface oxygen atoms of MoO₂ to generate Mo-OH Brönsted acid sites [23].

Fig. 7A and B show the ESR signals of MoO_3 and Pt/MoO_3 catalysts, when the catalysts were outgassed at room temperature and 673 K, followed by heating in the presence of hydrogen at different temperatures. The outgassed spectra exhibit a main (tetra)-coordinated Mo^{5+} signal at g=1.917 [35,36]. The introduction of hydrogen molecules at room temperature followed by

heating at 323 K decreased the ESR signal from Mo^{5+} species. The reduction of the signal might be due to the trapping of electrons by electron-deficient metals which were released from hydrogen atoms. The change in signal g=1.917 for MoO₃ and Pt/MoO₃ was observed upon each heating temperature. For MoO₃, there was a small decrease at *g*-value of 1.917, while the Pt/MoO₃ catalyst showed a gradual decrease in the intensity of the signal indicating that the formation of electrons occurs more extensively on the Pt/MoO₃ than on MoO₃.

Cumene cracking is known to be the probe reaction on Brønsted acid site. Shishido and Hattori have reported that the presence of spilt-over hydrogen drastically promoted cumene cracking over Pt/SO₄^{2–}-ZrO₂ [7]. They suggested that the protonic acid site originated by spilt-over hydrogen can be estimated qualitatively by cumene cracking activity under hydrogen flow. Fig. 8A shows the catalytic activity of MoO₃ and Pt/MoO₃ for cumene hydrocracking as a function of reaction temperature. The reaction was performed at the temperature range of 323-573 K under a hydrogen atmosphere. The product distributions of cumene hydrocracking over MoO₃ and Pt/MoO₃ catalysts are summarized in Table 1. The predominant component was propylene, while the minor components were benzene, toluene and ethylbenzene that composed the outlets of cracking. Fig. 8A shows that Pt/MoO₃ exhibited a higher rate of conversion compared to MoO3 for all reaction temperature ranges. The high activity of Pt/MoO₃ was most probably due to the ability of catalysts to form Brönsted (Mo-OH) which thereby produce acidic Brönsted $(MoO_x)^-(H_y)^+$ at a wide range of reaction temperature in the presence of Pt metals and Lewis acidic centers at $1585 + 1605 \text{ cm}^{-1}$. In fact, no acidic Brönsted $(MoO_x)^-(H_y)^+$ was formed on Pt-free MoO₃ which led to lower the activity of catalyst. The activity of MoO₃ may be related to the presence of MoO₂ phase which act as active sites for the cumene catalytic cracking [12]. This revealed the indispensability of active sites for the adsorption-dissociation of molecular hydrogen, such as Pt and the Lewis acidic centers for stabilizing electrons. The difference was extensively observed at a higher temperature due to the higher interaction of molecular hydrogen and Pt sites to form the acidic Brönsted $(MoO_x)^-(H_y)^+$ phase. In addition, the formation of lower alkanes was slightly suppressed at a higher temperature due to the alteration of the reaction mechanism. At higher temperatures,

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8-16



Fig. 8. (A) Effect of reaction temperature on cumene cracking over catalysts at 323–573 K. (B) Cumene cracking reaction over $MoO_3(\bullet, \bigcirc)$ and $Pt/MoO_3(\blacksquare, \square)$ catalysts at 573 K in the presence of hydrogen (black symbol) and nitrogen (white symbol).

able 1	
roduct distribution of cumene cracking over MoO_3 and Pt/MoO_3 in the range of 323–573	K.

Reaction temperature (K)	Selectivity (%)						
	MoO ₃			Pt/MoO ₃			
	Propylene	Benzene	Toluene and ethylbenzene	Propylene	Benzene	Toluene and ethylbenzene	
323	0	0	0	100	0	0	
373	0	0	0	100	0	0	
423	85	14.9	0.1	89.5	10.3	0.2	
473	69.3	25.8	4.9	76.7	17	6.3	
523	55	32.6	12.4	64.4	20.6	14.9	
573	48.6	36.2	15.2	58.8	22.5	18.7	

larger numbers of acidic Brönsted $(MoO_x)^-(H_y)^+$ suppressed the hydrogenolysis process and promoted the dimerization-cracking route to form relatively higher hydrocarbons [32]. The activity of both catalysts was low under nitrogen atmosphere at 573 K. In fact, the activities were thirteenfold and seventeenfold lower than those under hydrogen for MoO₃ without and with Pt (Fig. 8B). The low activity may be caused by the absence of acidic Brönsted $(MoO_x)^-(H_y)^+$ from molecular hydrogen during the reaction. Studies of cumene cracking have been reported by Shishido and Hattori over Pt/SO₄^{2–}–ZrO₂ [37]. High activity of cumene cracking on Pt/SO₄²⁻-ZrO₂ at 423 and 473 K has been reported due to the formation of protonic acid sites through hydrogen spillover mechanism. The higher activity was observed at a higher temperature due to the ease of adsorption-dissociation of hydrogen over Pt sites. Also, studies of the MoO₃ type catalyst for light alkane isomerization have been carried out by Matsuda [17] and Al-Kandari et al. [21,22]. Al-Kandari et al. pointed out that balanced metal-acid in the MoO_{2-x} (OH)_y phase is an active site for *n*-hexane and *n*-pentane isomerization. Matsuda et al. reported that H₂-reduced Pt/MoO₃ shows the highest activity of heptane isomerization due to the formation of acidic MoO_xH_y. Wehrer and co-workers also reported that the MoO₂ phase is an inefficient catalyst for skeletal isomerization of alkane [13,15]. Consistently, our results showed that Pt/MoO₃, which possesses acidic Brönsted $(MoO_x)^-(H_y)^+$, exhibited high catalytic activity in cumene hydrocracking with 54.8 kJ/mol of apparent activation energy (Fig. 9). The activation energy of cumene cracking over Pt/MoO₃ was slightly lower than that of MoO₃ and differed markedly to the HY and HX

catalysts for which the activation energy is 78.58 and 97.99 kJ/mol, respectively [38]. The low activation energy for Pt/MoO₃ indicated the easiness of acidic Brönsted $(MoO_x)^-(H_y)^+$ to interact with the reactant in order to initiate the cracking.



Fig. 9. Arrhenius plot of $\ln k$ in the effect of reaction temperature on MoO₃ (\bullet) and Pt/MoO₃ (\blacksquare) in the range of 473–573 K.

S.N. Timmiati et al. / Applied Catalysis A: General 459 (2013) 8–16

4. Conclusion

2,6-Lutidine adsorbed IR study indicated that MoO3 and Pt/MoO₃ possessed dual doublet absorption bands at 1660+1640 and $1650 + 1630 \text{ cm}^{-1}$, which associated with 2,6-lutidinium cations adsorbed on the -OH defect structure and Brönsted Mo-OH on the surface of MoO₃. Also, the doublet bands at 1605 + 1585 cm⁻¹ were found to correspond to the Lewis acid sites. Both Brönsted and Lewis acidic sites are strong in which the 2,6-lutidine remains on both acidic centers after outgassing at 473 K. While the formation of active acidic Brönsted $(MoO_x)^-(H_y)^+$ phase over Pt/MoO₃ was confirmed based on the results of XRD and hydrogen adsorption on 2,6-lutidine pre-adsorbed IR studies, no acidic Brönsted $(MoO_x)^-(H_y)^+$ phase was observed on Pt-free MoO_3 indicating the indispensability of Pt active sites for adsorptiondissociation of molecular hydrogen. The presence of an acidic Brönsted $(MoO_x)^-(H_y)^+$ phase enhanced the conversion rate of cumene cracking over Pt/MoO₃ by about twofold higher than that on MoO₃.

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References

- [1] G. Larsen, E. Lotero, S. Raghavan, R.D. Parra, C.A. Querini, Appl. Catal. A: Gen. 139 (1996) 201-211.
- [2] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal. 181 (1999) 57-72.
- [3] T. Matsuda, H. Sakagami, N. Takahashi, Catal. Today 81 (2003) 31-42.
- [4] K. Ebitani, J. Konishi, H. Hattori, J. Catal. 130 (1991) 257-267.
- K. Ebitani, J. Tsuji, H. Hattori, H. Kita, J. Catal. 135 (1992) 609-617.
- [6] M. Guesnet, P. Magnoux, D. Martin, Stud. Surf. Sci. Catal. 111 (1997) 1-19.

- [7] T. Shishido, H. Hattori, Appl. Catal. A: Gen. 146 (1996) 157-164.
- [8] S. Triwahyono, T. Yamada, H. Hattori, Appl. Catal. A: Gen. 242 (2003) 101–109. [9] E.A. Blekkam, C. Pham-Huu, M.J. Ledoux, J. Guille, Ind. Eng. Chem. Res. 33 (1994)
- 1657 1664[10] C. Pham-Huu, P.D. Gallo, E. Peschiera, M.J. Ledoux, Appl. Catal. 132 (1995) 77–96.
- [11] A.P.E. York, C. Pham-Huu, P.D. Gallo, E.A. Blekkam, M.J. Ledoux, Ind. Eng. Chem. Res. 35 (1996) 672-682
- [12] A. Katrib, A. Benadda, J.W. Sobczak, G. Maire, Appl. Catal. A: Gen. 242 (2003) 31 - 40
- [13] P. Wehrer, S. Libs, L. Hilaire, Appl. Catal. A: Gen. 238 (2003) 69-84.
- [14] P. Wehrer, C. Bigey, L. Hilaire, Appl. Catal. A: Gen. 243 (2003) 109–119. [15] P. Wehrer, L. Hilaire, E. Petit, Appl. Catal. A: Gen. 273 (2004) 249-258.
- [16] T. Matsuda, Y. Hirata, H. Itoh, H. Sakagami, N. Takahashi, Microporous Meso-
- porous Mater. 42 (2000) 337-344. [17] T. Ohno, Z. Li, N. Sakai, H. Sakagami, N. Takahashi, T. Matsuda, Appl. Catal. A: Gen. 389 (2010) 52-59.
- [18] T. Matsuda, A. Hanai, F. Uchijima, H. Sakagami, N. Takahashi, Microporous Mesoporous Mater. 51 (2002) 155-164.
- [19] T. Matsuda, T. Ohno, Y. Hiramatsu, Z. Li, H. Sakagami, N. Takahashi, Appl. Catal. A: Gen. 362 (2009) 40-46.
- [20] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Catal. Commun. 9 (2008) 847-852.
- [21] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Appl. Catal. A: Gen. 383 (2010) 141–148.
 [22] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Appl. Catal. A: Gen. 361 (2009) 81–85.
- [23] H. Al-Kandari, A.M. Mohamed, S. Al-Kandari, F. Al-Kharafi, G.A. Mekhemer, M.I. Zaki, A. Katrib, J. Mol. Catal. A: Chem. 368/369 (2013) 1-8.
- [24] S. Triwahyono, Z. Abdullah, A.A. Jalil, J. Nat. Gas Chem. 15 (2006) 247-252.
- [25] M.J. Ledoux, C. Pham-Huu, P. Delporte, E.A. Blekkam, A.P.E. York, E.G. Derouane, A. Fonseca, Stud. Surf. Sci. Catal. 92 (1994) 81-86.
- [26] P. Delporte, F. Meunier, C. Pham-Huu, P. Vennegues, M.J. Leduox, J. Guille, Catal. Today 23 (1995) 251-267.
- [27] D.T. Hawkins, W.L. Worrel, Metall. Trans. 1 (1970) 271-273.
- [28] Corma, C. Rodellas, V. Fornes, J. Catal. 88 (1984) 374-381.
- [29] N.N. Ruslan, N.A. Fadzlillah, A.H. Karim, A.A. Jalil, S. Triwahyono, Appl. Catal. A: Gen. 406 (2011) 102-112.
- [30] A.M. Turek, I.E. Wachs, E. DeCanio, J. Phys. Chem. 96 (1992) 5000-5007.
- S. Triwahyono, T. Yamada, H. Hattori, Catal. Lett. 85 (2003) 109-115. [31]
- [32] H.D. Setiabudi, A.A. Jalil, S. Triwahyono, J. Catal. 294 (2012) 128-135.
- [33] A.H. Karim, S. Triwahyono, A.A. Jalil, H. Hattori, Appl. Catal. A 433/434 (2012) 49-57.
- [34] S. Triwahyono, A.A. Jalil, S.N. Timmiati, N.N. Ruslan, H. Hattori, Appl. Catal. A: Gen. 372 (2010) 103-107.
- [35] M. Occhiuzzi, D. Cordishi, R. Dragone, J. Phys. Chem. 106 (2002) 12464-12469.
- [36] Z. Sojka, M. Che, Surf. Chem. Catal. 3 (2000) 163-174.
- [37] T. Shishido, H. Hattori, J. Catal. 161 (1996) 194-197.
- [38] A.H.A.K. Mohammed, S.k. Dhidan, M.H. Al-Hassani, J. Eng. 15 (2009) 4107-4121.

16